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Microwave Assisted, Fly Ash Catalyzed Synthesis of Coumarin Derivatives: Green Approach

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ABSTRACT

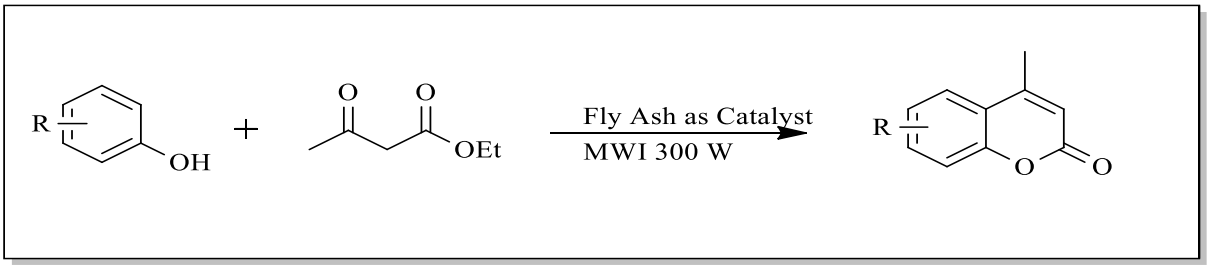
Solvent free synthesis of substituted Coumarin by Von Pechmann condensation of phenols with β-ketoesters catalyzed by fly ash as a byproduct from thermal power station by microwave irradiation method. Our present protocol is economical and clean comprise of green reagent, solvent and catalyst.

Keywords: Pechmann Condensation; Coumarin; MWI; Green Synthesis

INTRODUCTION

Coumarins [1] and their various derivatives has attracted considerable attention of medicinal and organic chemist from many years, due to its large number of pharmaceutical activities like anti-bacterial [2], anti-cancer [3], anti-coagulant, anthelmintic, hypnotic, optical brighteners [4], anti-inflammatory and anti-HIV activities [5].

The representative synthetic routes of Coumarin and its derivatives include Pechmann [6], knoevenagel [7], Perkin [8], Reformatsky [9] and Wittig [10] condensation reactions. Among these, Pechmann condensation is one of the most widely used method for synthesis of Coumarin. Acid catalyst have been used in the Pechmann [6] reaction including use of simple starting materials that is phenol and β-ketoesters in the presence of variety of acidic agents, such as chlorosulfonic acid [11], Sulfuric acid [6], melamine formaldehyde resin supported H+ ion catalyzed [12], ionic liquid catalyzed [13], oxalic acid catalyzed [14], silica triflate catalyzed, heterogeneous catalyst, zirconia supported catalyst etc (Scheme 1).



Scheme 1: Synthesis of Coumarin Derivatives

Fly ash is mainly consist of the components of vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) and calcium oxide (CaO), the main mineral compounds in coal-bearing rock. It has found very vast applications in many reactions such as, rearrangement reaction, condensation reaction, usually acts as strong Lewis acid catalyst and dehydrating agent [15-18] (Tables 1 and 2).

Table 1: Solvent free synthesis of Coumarins catalyzed by fly ash in microwave irradiation method (300W)

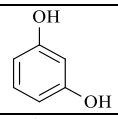
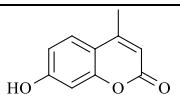
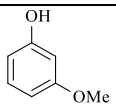
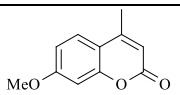
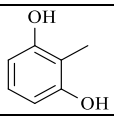
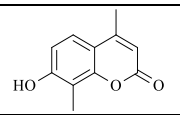
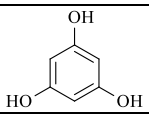
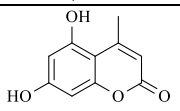
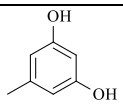
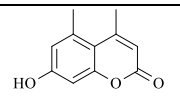
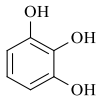
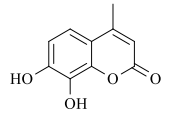
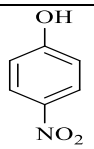
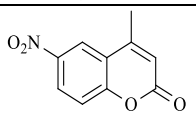
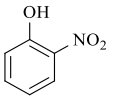
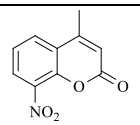
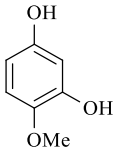
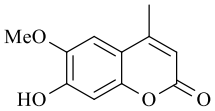
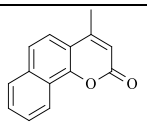
Substrate	Product	Time in Sec.	M. P. in °C		Yield[a] (%)
			Obs.	Lit	
		60	184-86	185[14]	98
		60	158-60	161[14]	95
		60	138-39	138[14]	90
		60	285-86	285[14]	90
		60	257-58	258[14]	92
		80	235-36	237[14]	89
		110	147-49	150[14]	72
		100	183-184	185[14]	79
		90	164-165	165[14]	91
		120	156-158	155[14]	87
[a]Isolated Yield					

Table 2: Optimization of reaction condition for synthesis of coumarin under microwave irradiation technique at low power (300W) using fly ash as catalyst[b]

Entry	Catalyst	Mol %	Yield[a]
1	Fly Ash	0	--
2	Fly Ash	5	stress
3	Fly Ash	10	40%
4	Fly Ash	15	59%
5	Fly Ash	**20**	**98%**
6	Fly Ash	25	93%
7	Fly Ash	30	88%
[b]Reaction Condition: Resorcinol (**10mmol**), Ethyl acetoacetate (**10mmol**) and fly ash (**20 mol %**), MWI 300W [a]Isolated Yield			

EXPERIMENTAL

General experimental procedure for synthesis of 7-hydroxy-4-methylcoumarins

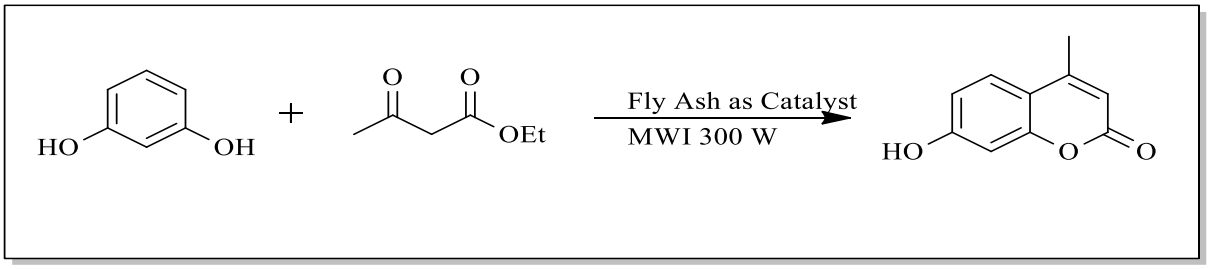
A mixture of resorcinol (**10mmol**), ethyl acetoacetate (**10mmol**) and fly ash (**20 mol %**) were subjected to microwave irradiation at 300W for appropriate time (**Table 1**). After completion of reaction, as monitor by TLC, the reaction mixture was cooled to room temperature, water was added and stirred for another two minutes, and precipitation was filtered off and recrystallized from methanol to afford pure 7-hydroxy-4-methylcoumarins as yellowish prism.

7-hydroxy-4-methylcoumarins

yield 98 %, mp 184-186 °C. ^{1}H NMR ($CDCl_3$) δ: 2.2 (s, 3H, Me), 6.1 (s, 1H), 6.83 (d, 1H, *J* 2.4 Hz), 6.97 (dd, 1H, *J* 8.7 and 2.4 Hz), 7.5 (d, 1H, *J* 8.7 Hz). IR (KBr, ν/cm^{-1}): 2985, 1740, 1625. ES/MS, *m/z*: 175 (M-H).

RESULTS AND DISCUSSIONS

In summary, it can be stated that, the present protocol for synthesis of Coumarin by Pechmann condensation is highly efficient as it avoid use of organic solvents at any stage of reaction, under microwave irradiation technique at very low power (300W) and presence of fly ash as a byproduct from thermal power station as a catalyst (Scheme 2).



Scheme 2: Model Reaction for Synthesis of Coumarin Derivatives

A mixture of substituted phenols and ethyl acetoacetate was subjected to microwave irradiation of very low power (300W) in presence of fly ash under solvent free condition (Scheme 1). The Progress of reaction was checked by chromatography (TLC). Optimization of reaction condition was achieved by using varying amounts of fly ash catalyst and best results of yields could be obtained by using 20 mol % of catalyst (Table 2).

CONCLUSION

Herein, we report the Pechmann condensation reaction of phenols and β-ketoesters using fly ash as a simple, efficient, easily available as a catalyst under microwave irradiation method and solvent free condition (Scheme 1). We carried out a series of substituted phenols with ethyl acetoacetate to obtain corresponding Coumarin derivatives in very good to best yield (Table 1).

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Conflicts of Interest

The authors declared no conflict of interest.

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